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## Preconcentration Modeling for the Optimization of a Micro Gas Preconcentrator Applied to Environmental Monitoring.

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### Abstract:

This paper presents the complete modeling of the preconcentration cycle for the optimization of a Micro Gas Preconcentrator applied to atmospheric pollution monitoring. The particularity of this modeling is based on the fact that it includes all equations governing not only the adsorption and desorption phenomena but also the detection phase. Two different approaches based on kinetic equations were used to illustrate the behavior of the Micro Gas Preconcentrator for given experimental conditions. The need of a high adsorption flow and heating rate, a low desorption flow and detection volume is demonstrated through this paper.

### Keywords:

*Preconcentration modelling; Micro Gas Preconcentrator; Adsorption; Breakthrough time; desorption; detection*

### I. Introduction:

In our previous studies, a micro Gas Preconcentrator for the detection of volatile organic Compounds (VOCs) in trace level has been developed [1, 2]. During these studies, we observed that the efficiency of this device was closely linked to four keys parameters such as the adsorption and desorption flow rates, desorption heating rate and detection volume; hence the idea to optimize these parameters through a complete modeling of the preconcentration from few experiments. Different couples of adsorbent-adsorbed gas can be simulated in order to predict the behavior of our device when it is used in these conditions. In addition, this modeling allows as much to determine the breakthrough time [3, 4] as to describe the desorption peak aspect and therefore to quantify the preconcentration performance. The particularity of this modeling is related to the fact that it treats the preconcentration system as an ensemble where the current models [5, 6, 7] propose only to treat separately the adsorption with the desorption or the detection.

### II. Theory and definition about the preconcentration performance

It is very difficult to define a preconcentration factor since, for a given preconcentrator, it is closely related to these four external parameters. We can define a theoretical preconcentration factor which will be the ratio between the volume of gas passing through the micro-device during the adsorption phase and the volume of this micro-device. It is a theoretical maximum which can be approached with very low detection volume such as a micro gas chromatograph. Nevertheless, with the experimental results, we will measure a “practical” preconcentration factor defined as an amplification factor given by the ratio

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between the maximum of concentration measured during the desorption phase and the concentration of the injected gas.

The choice of different adsorption and desorption flow rates is of importance since the mass conservation between absorbed and desorbed quantities leads to the equation  $C_1 \cdot d_1 \cdot t_1 = C_2 \cdot d_2 \cdot t_2$  in which C, d and t are respectively the concentration, the flow rate and the duration of the adsorption (1) and desorption phase (2). At this end, a high flow rate during the adsorption (limited by pressure drop) and a low one during desorption (limited by the fact that many detectors modify the measured gas) were needed.

### III. Modeling algorithm

#### III.1. Adsorption and Breakthrough time

The first step of this modeling consists in describing numerically the adsorption phenomenon which can be extended to the breakthrough time prediction. For the prediction of the breakthrough time, two approaches are possible; the first one, more general, deriving from Langmuir or BET (in case of  $P \ll P_0$ , with P and  $P_0$  respectively the atmospheric pressure and the saturation vapor pressure) isotherms is described by a homographic function of the

concentration C:  $T_b = \frac{\alpha N_0}{d \cdot (1 + \alpha C)}$  with  $\alpha$  a constant and  $N_0$  the number of accessible

adsorption sites. So, there are two limit cases: on one hand, the strong adsorbent materials with  $\alpha C \gg 1$  leading to a breakthrough time proportional to  $\frac{1}{C}$  and on other hand, the poor adsorbent materials represented by the limit case of  $\alpha C \ll 1$  which leads to a constant breakthrough time.

The second approach considers only the high adsorbent materials by supposing a constant adsorption capacity (Langmuir with high concentration or Dubinin) and it is defined with a hyperbolic function of the concentration as previously in limit case of  $\alpha C \gg 1$ .

These models compared with our experimental results have given a good correlation particularly the BET and Langmuir models which reproduce closely the experimental points (Figure 1).

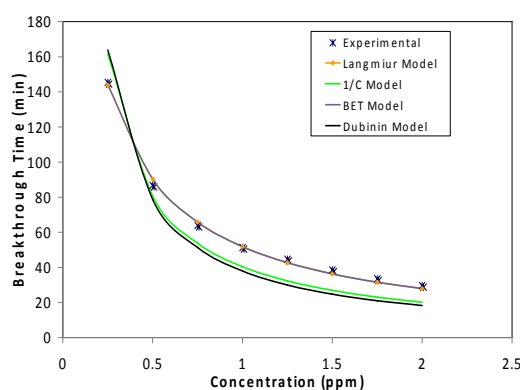
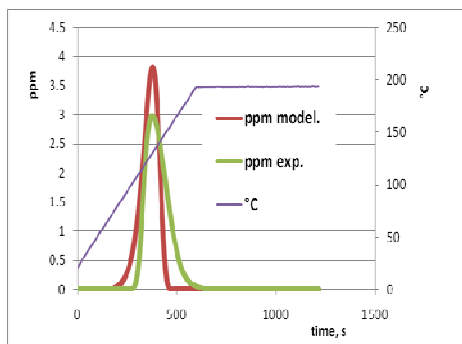


Figure 1: Comparison between experimental breakthrough time and theoretical models (BET, Dubinin, Langmuir and 1/C) for 10 mg of carbon.

#### III.2. Desorption

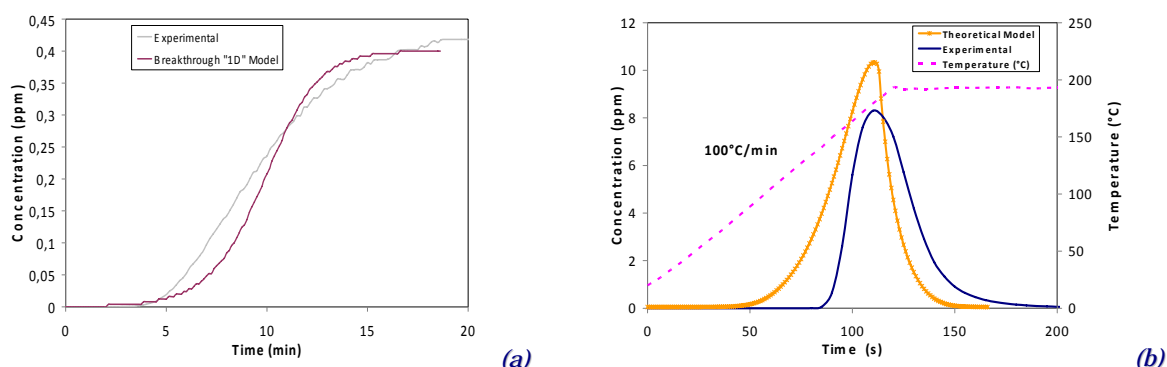
The second part of this work has been dedicated to the prediction of the shape of the desorption peak. Previously, Joly *et al.* [7] have developed this kind of model with finite elements, but they were limited only to stationary state. In order to complete and extend this work to the non stationary state, we tried to implement a kinetic model based on finite differences using Langmuir hypotheses. Two different versions have been developed: on one hand, a simple zero dimension modeling ("0D" no spatial variable, only time) considering the preconcentrator as a homogenous box was implemented within Microsoft Excel. This model

includes the delay time due to the detection volume and the interaction between the detector and the gas. It not only confirms the decrease of detected concentration when the flow rate is increased but also reproduces correctly the appearance of the experimental desorption peak realized in same conditions (Figure 2). However, this model does not allow predicting the breakthrough curve.



*Figure 2: Comparison between experimental and theoretical results of a desorption, Excel "OD" model.*

On other hand, a one spatial dimension model ("1D") has been implemented with LabVIEW. In addition to adsorption-desorption kinetics, this model includes the equations of transport and distribution and predicts as much the adsorption and breakthrough curve as the desorption peak (Figures 3 and 4). So, it should be noted that the small difference between the experimental desorption peak and the model one is associated to the difficulty of measuring the real temperature of the adsorbent material during the desorption phase since the thermocouple is placed outside the micro-device.



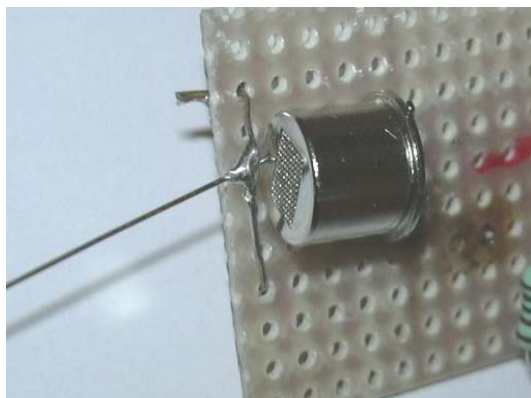
*Figure 3: (a) Breakthrough phase with 400 ppb of benzene: comparison between experimental and theoretical results, "1D" Labview model ; (b) Desorption phase: comparison between experimental and theoretical results for heating rate of 100°C/min after adsorption of 250 ppb of benzene during 5min, "1D" Labview model.*

However, the precision of this desorption model is essentially associated to the detection system used for the measurement of the concentration; therefore, its modeling is so crucial to improve our preconcentration model.

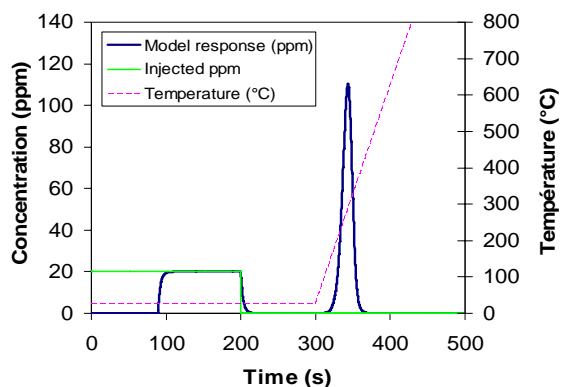
### III.2. Detection system

The last part of this modeling concerns the influence of the detection volume. The volume of the detector  $v$  acts as low-pass filter with a constant time of  $\frac{d}{v}$  reducing considerably the response of the detector. This is why we have integrated, for our experiments, the outlet of the preconcentrator in the sensor packaging (Figaro type 2620) in order to reduce considerably the detection volume (Figure 5).

And finally, all these parts have been assembled to obtain a unique model describing the complete preconcentration process for given experimental conditions (Figure 6).



*Figure 5: Figaro sensor with micro-channel capillary connected through its packaging*



*Figure 6: Complete model describing all the preconcentration cycle.*

## V. Conclusion

The good correlation between theoretical model and complete experimental preconcentration cycle obtained with a Micro Gas Preconcentrator has been demonstrated. This model will allow to predict the behavior of preconcentrators for many adsorbent - adsorbed gas couples (carbon-benzene, carbon-toluene, carbon nanotubes-benzene, carbon nanotubes-nitrobenzene, Tenax-xylene...) in any experimental condition with only two experiments to determine the keys kinetic parameters (activation energy, frequency factor) to include in the modeling. However, the implemented models cannot describe all adsorption forms because it is essentially based on a monolayer adsorption model. Therefore, a multilayer adsorption model including different adsorption sites is underway in order to cover a more large range of adsorbent-adsorbed gas couples.

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